filtered and evaporated to dryness to give 41.7 g. of light yellow oil. Heating at 180° under a pressure of 20 to 25 mm. resulted in the decomposition of the unreacted IV into butadiene and sulfur dioxide. When the evolution of gases had ceased, heating was discontinued. Recrystallization of the residue from a mixture of benzene and petroleum ether gave 20.5 g. (41%) of pure white needles of 2,3-dihydrothiophene 1-dioxide (XII), m.p. 48–49° (reported[22] 48.5–49.5°).

3-Dimethylaminotetrahydrothiophene 1-Dioxide Picrate (XIII). A. From 2,3-Dihydrothiophene 1-Dioxide (XII).—A solution of 0.50 g. (0.0042 mole) of 2,3-dihydrothiophene 1-dioxide (XIII) in 10 ml. of dry benzene and 1.90 g. (0.042 mole) of dimethylamine were placed in a tightly stoppered flask. After standing for 4 days at room temperature the solution was evaporated to near dryness, taken up in chloroform, and extracted with 5% hydrochloric acid. The acidic aqueous solution was cooled to 0° and made basic with sodium hydroxide and again extracted with chloroform. The chloroform extracts were combined, dried over magnesium sulfate, filtered and evaporated to dryness under vacuum at room temperature to give 0.65 g. (93%) 3-dimethylaminotetrahydrothiophene 1-dioxide (XI) as a very light yellow oil which could not be induced to crystallize. It was therefore converted into a picrate, by the method of Shriner and Fuson.[21] Recrystallization from an ethanol–water mixture produced the pure picrate of 3-dimethylaminotetrahydrothiophene 1-dioxide (XIII), m.p. 193–194° (without decomposition).

Anal. Calcd. for $C_{12}H_{16}N_4O_9S$: C, 37.19; H, 4.08. Found: C, 37.01; H, 3.90.

B. **From 3-Dimethylamino-2,3-dihydrothiophene 1-Dioxide (VIII).**—A solution of 0.50 g. (0.0031 mole) of 3-dimethylamino-2,3-dihydrothiophene 1-dioxide (VIII) in 50 ml. of glacial acetic acid plus 0.1 g. of prereduced PtO_2 catalyst was subjected to low pressure hydrogenation. The hydrogen uptake was 60.2 ml. (86% of theory) in 12 hours. The catalyst was filtered off and 10 ml. of a saturated solution of picric acid in 95% ethanol was added to the filtrate. The resulting precipitate was purified by four recrystallizations from dilute ethanol to give the picrate of 3-dimethylaminotetrahydrothiophene 1-dioxide (XIII), m.p. 193–194°. A mixed melting point with the picrate XIII, prepared from XII in part A above, showed no depression, melting at 193–194°.

3-Dimethylamino-2,3-dihydrothiophene 1-Dioxide Methiodide (XIV).—A solution of 72.5 g. (0.450 mole) of 3-dimethylamino-2,3-dihydrothiophene 1-dioxide (VIII) in 200 ml. of absolute alcohol was placed in a 500-ml. flask, equipped with a reflux condenser protected with a drying tube, and 64.5 g. (0.454 mole) of methyl iodide was added. Crystalline material formed almost immediately and the reaction mixture boiled vigorously for a few minutes. The reaction mixture was allowed to stand for 1.5 hours and then cooled to 0°. The cold mixture was filtered, washed with 100 ml. of cold alcohol and then with peroxide-free ether to give 116.5 g. of XIV. An additional 9.5 g. of XIV could be obtained by working up the mother liquors and washings. Recrystallization from ethanol gave 125 g. (96%) of 3-dimethylamino-2,3-dihydrothiophene 1-dioxide methiodide (XIV) as pure white microcrystals, m.p. 184–185° dec.

Anal. Calcd. for $C_7H_{14}INO_2S$: C, 27.72; H, 4.63; N, 4.62; I, 41.86. Found: C, 27.85; H, 4.50; N, 4.77; I, 42.11.

Thiophene 1-Dioxide (I).—A solution of 10.0 g. (0.033 mole) of 3-dimethylamino-2,3-dihydrothiophene 1-dioxide methiodide (XIV) in 150 ml. of distilled water was placed in a 300-ml., two-necked flask, fitted with a mechanical stirrer and powder funnel, and cooled to 0–5°. This resulted in the crystallization of a considerable amount of XIV. However, since the decomposition reaction went to completion rapidly no further addition of water was made, because of the desirability of keeping the final volume of the aqueous phase as small as possible for extraction purposes. The addition of freshly prepared silver oxide suspension from 11.22 g. (0.066 mole) of silver nitrate to this mixture, during a 15-minute period, resulted in the instantaneous liberation of trimethylamine. The reaction was allowed to proceed for an additional 15 minutes while the temperature was maintained between 0–5°. It was then filtered through a buchner funnel, containing ice, into an ice-cooled flask (no appreciable amount of iodide ion was present in either the residue or filtrate). The filtrate was transferred to a separatory funnel, also containing ice, and extracted with chloroform. The chloroform extracts were collected in an erlenmeyer flask, dried over magnesium sulfate, and used in this form for all subsequent reactions.

COLLEGE PARK, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE UNIVERSITY]

Cyclic Dienes. IV. The Dimerization of Thiophene 1-Dioxide[1,2]

BY WILLIAM J. BAILEY[3] AND EARL W. CUMMINS

RECEIVED AUGUST 6, 1953

In concentrated solution even below room temperature, thiophene 1-dioxide (I) dimerizes by a Diels–Alder reaction with the loss of sulfur dioxide to form 3a,7a-dihydrobenzothiophene 1-dioxide (II). The structure of II was proved by ultraviolet absorption, hydrogenation and independent synthesis of the hydrogenation product. Bromination of I proceeds very slowly to give bromination products of both I and II, indicating that I exists in solution largely as a monomer and not as a dissociating dimer.

Thiophene 1-dioxide (I) was synthesized[2] in order to determine whether it was aromatic or aliphatic. It was found, however, that it could not be isolated in a pure state. All attempts to obtain a concentrated form of the dioxide I, even at low temperatures, resulted in a spontaneous decomposition with the liberation of sulfur dioxide. From the reaction mixture was isolated a white crystalline solid II that analyzed for $C_8H_8O_2S$. II absorbed 3 moles of hydrogen to yield a saturated sulfone III. The similarity of the ultraviolet absorption spectrum of II, which indicates an ϵ maximum of 3550 at 266 mμ and an ϵ minimum of 1260 at 228 mμ, with that of cyclohexadiene-1,3 suggests the presence of conjugated double bonds in a six-membered ring. Thus II can be represented as 3a,7a-dihydrobenzothiophene 1-dioxide and III as octahydrobenzothiophene 1-dioxide. The formation of II can be rationalized by assuming that I dimerized with one molecule acting as the diene and the other as a dienophile to form the unstable Diels–Alder adduct IV, which spontaneously lost the bridged sulfone group to form II. The structure of III was proved by independent synthesis. Butadiene (V) was added to 2,3-dihydrothiophene 1-dioxide (VI) to produce Δ^5-hexahydrobenzothiophene 1-dioxide (VII). Hydrogenation of VII produced the octa-

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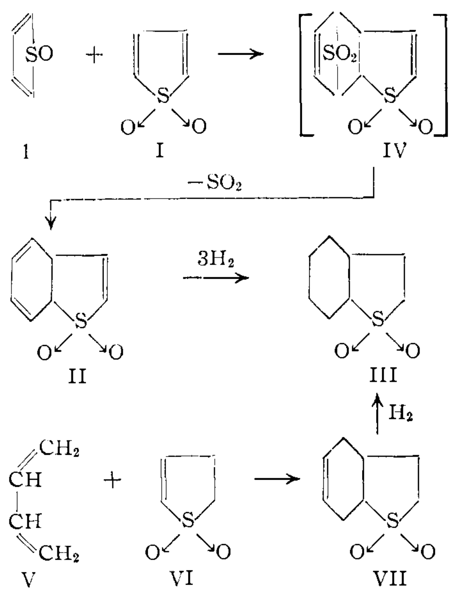
[2] Previous paper in this series, THIS JOURNAL, **76**, 1932 (1954).

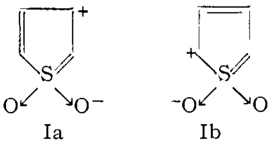
[3] Department of Chemistry, University of Maryland, College Park, Maryland.

hydro derivative (III), which did not depress the melting point of the product obtained from the dimer II.

DIAGRAM I



The ease with which thiophene 1-dioxide (I) undergoes dimerization suggests that there is little or no stabilization of this ring system. This lack of aromatic properties can be rationalized by two different concepts. Since the dioxide possesses only four electrons in the ring, it lacks the $(2 + 4n)$ or 6π electrons necessary for aromatic resonance according to Huckel.[4] Using another approach, it must be assumed for aromatic stabilization that the resonance structures similar to Ia and Ib must be important. In both these



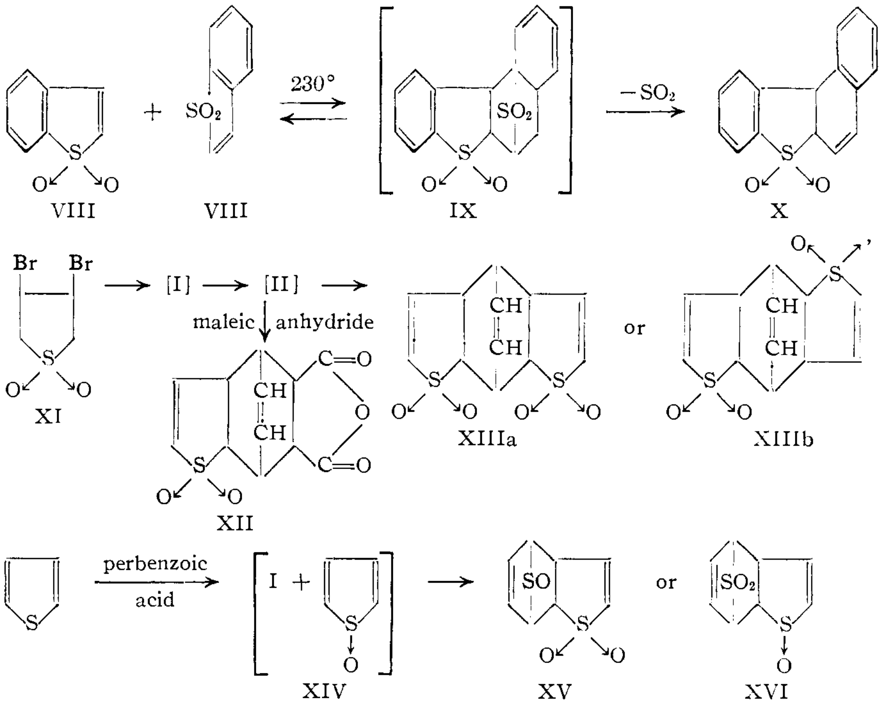
structures sulfur has expanded its valence shell to ten electrons. It can be said, therefore, that if resonance is possible with 4π electrons, the energy necessary to expand the valence shell of sulfur is less than the resonance energy that would be gained from the ring.

In the dimerization reaction thiophene 1-dioxide (I) resembles cyclopentadiene, which readily forms dicyclopentadiene,[5] or derivatives of the unknown cyclopentadienone such as 3,4-diphenylcyclopentadienone.[6] The dimer of the latter on heating loses the bridged carbonyl group to produce the 2,2a,4,5-tetraphenyl-2a,6a-dihydroindenone. This latter example would indicate that the thiophene 1-dioxide (I) ring is slightly more stable than the cyclopentadienone ring, since 3,4-diphenylthiophene 1-dioxide[7] is a stable monomer under similar conditions.

Since the present work was originally presented,[1] Bordwell, McKellin and Babcock[8] reported that benzothiophene 1-dioxide (VIII) dimerized at 230° to produce the unstable adduct IX, which lost sulfur dioxide to give 6a,11b-dihydronaphtho-(2,1-b)-benzo(d)thiophene 1-dioxide (X). This work clearly indicates the stabilizing effect of the benzene ring on the thiophene 1-dioxide ring. Bordwell and McKellin[9] had previously concluded from the addition reactions to the double bond in VIII that the thiophene dioxide ring was not aromatic but behaved more like an α,β-unsaturated sulfone.

Also since the present work was presented,[1] Backer and Melles[10] reported the synthesis of two derivatives of II.

Treatment of 3,4-dibromotetrahydrothiophene 1-dioxide (XI) with pyridine produced a solution of thiophene 1-dioxide (I). Addition of maleic anhydride to this solution produced the Δ^2-hexahydro-4,7-endovinylene-5,6-benzothiophenedicarboxylic anhydride 1-dioxide (XII). Upon standing, the solution of dioxide I did not yield II but produced a trimeric material which was assigned the



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[4] E. Huckel, *Z. Elektrochem.*, **43**, 752 (1937).

[5] G. Kraemer and A. Spilker, *Ber.*, **29**, 558 (1896).

[6] C. F. H. Allen and E. W. Spanagel, THIS JOURNAL, **55**, 3773 (1933).

[7] M. Lanfry, *Compt. rend.*, **154**, 519 (1912).

[8] F. G. Bordwell, W. H. McKellin and D. Babcock, THIS JOURNAL, **73**, 5566 (1951).

[9] F. G. Bordwell and W. H. McKellin, *ibid.*, **72**, 1985 (1950).

[10] H. J. Backer and J. L. Melles, *Proc. Koninkl. Nederland. Akad. Wetenschap.*, **54B**, 340 (1951); *C. A.*, **47**, 6932 (1953).

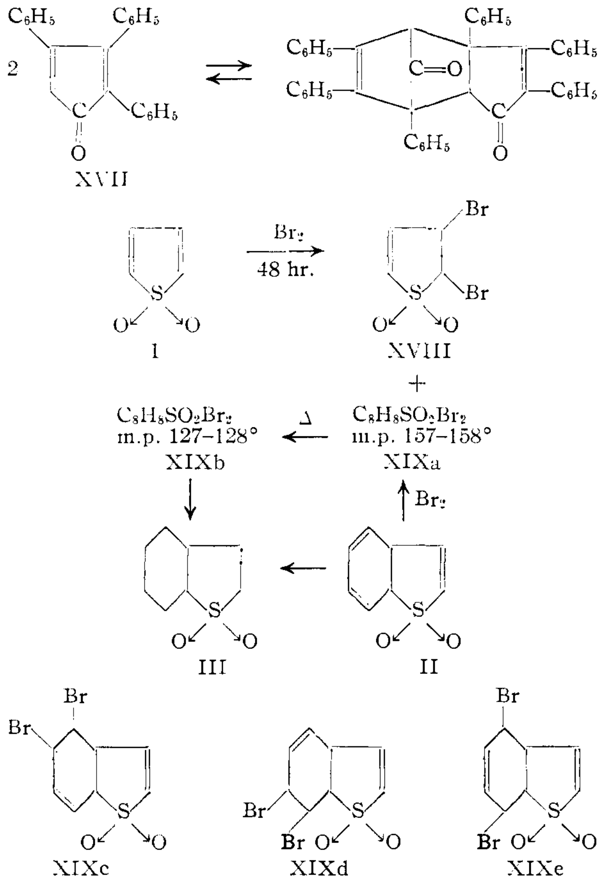
structure of $\Delta^{2,5}$-hexahydro-4,8-endovinylenebenzodithiophene 1,7-tetroxide (XIIIa) or its isomer XIIIb. Proof of the structure of XII and XIII was not given.

Subsequent work by the same authors[11] showed that oxidation of thiophene with perbenzoic acid apparently produced a solution of the sulfone I plus the sulfoxide XIV which combined to form the dimeric sesquioxide XV or XVI. Similar reactions were observed with substituted thiophenes but again a rigorous structure proof was omitted.

Since several derivatives of cyclopentadienone, such as 2,3,5-triphenylcyclopentadienone (XVII), exist in solution as dissociating dimers,[12] an attempt was made to determine if IV existed to any large extent in a solution of I. Although the absorption spectrum of I[2] can only be explained by assuming a large percentage of undissociated I in solution, the presence of a considerable quantity of IV cannot be ruled out.

Since the double bond in the bicycloheptene ring of dicyclopentadiene is quite reactive,[13] it was reasoned that the double bond in the bridged ring in IV would be more reactive toward bromine than the double bonds in I, and that if bromine did add to IV, the reaction product would be stable to a reverse Diels–Alder or loss of sulfur dioxide. A solution of I in chloroform adds bromine only very slowly at room temperature, indicating very little, if any, of IV present in the solution. If this solution was allowed to stand for 48 hours, the bromine was slowly absorbed and some sulfur dioxide eliminated to yield a mixture of products. From this mixture was isolated 2,3-dibromo-2,3-dihydrothiophene 1-dioxide (XVIII). The ultraviolet absorption spectrum of XVIII which increases to an ϵ of 4470 at 220 mμ is almost identical with that of 3-bromo-2,3-dihydrothiophene 1-dioxide.[2] Also from this mixture was isolated a dibromotetrahydrobenzothiophene 1-dioxide (XIXa), m.p. 157–158°. The structure of XIXa was indicated by analysis, molecular weight, ultraviolet absorption and an independent synthesis from II. Which of the three possible structures, XIXc, XIXd, XIXe, was produced in these two brominations was not determined. Heating a solution of XIXa produced a second isomeric dibromotetrahydrobenzothiophene 1-dioxide (XIXb), m.p. 127–128°. The structure of XIXb was indicated by analysis, molecular weight, ultraviolet absorption and hydrogenation to the known octahydrobenzothiophene 1-dioxide (III). Both XIXa and XIXb had identical absorption spectra, increasing from an ϵ of 70 at 280 mμ to an ϵ of 4470 at 220 mμ, indicating an α,β-unsaturated cyclic sulfone. The inability to isolate a bromination product of IV indicates that IV is merely a transient intermediate in the dimerization of I to form II.

DIAGRAM III



Experimental[14]

The Dimerization of Thiophene 1-Dioxide (I). 3a,7a-Dihydrobenzothiophene 1-Dioxide (II).—The methylene chloride solution of thiophene 1-dioxide (I),[2] resulting from the decomposition of 20 g. (0.066 mole) of 3-dimethylamino-2,3-dihydrothiophene 1-dioxide methiodide, was evaporated to dryness under a vacuum of 20 mm., while the pot temperature was maintained below 0°, to give a viscous light yellow oil. When this oil was allowed to warm up to room temperature, decomposition took place with the liberation of heat and copious amounts of sulfur dioxide. The residue that remained was a light yellow, hard rock-like mass and weighed 4.58 g.

Trituration of this solid with methylene chloride dissolved all but 1.43 g. of almost pure white solid. This insoluble portion darkened but did not melt when heated to 300°. It was presumed to be a polymer of I and was not further investigated.

The methylene chloride extracts were evaporated to dryness, under vacuum at room temperature, to give 2.82 g. of a light yellow crystalline solid. Recrystallization four times from an ether–petroleum ether mixture gave 1.88 g. (34% based on methiodide) of pure white needles of 3a,7a-dihydrobenzothiophene 1-dioxide (II), m.p. 90–91.5°. Care was taken to maintain the temperature as low as possible to prevent polymerization of II. It was found that heating a solution of II resulted in the formation of an amorphous precipitate. A sample of II darkened and became partially insoluble after standing at room temperature for 2 weeks.

Anal. Calcd. for $C_8H_8O_2S$: C, 57.14; H, 4.76; mol. wt., 168. Found: C, 57.19; H, 4.97; mol. wt. (cryoscopic in benzene), 161.

Δ^5-Hexahydrobenzothiophene 1-Dioxide (VII).—Using a modification of the procedure of Alder, Rickert and Windemuth,[15] butadiene (V) and 2,3-dihydrothiophene 1-dioxide (VI) were allowed to react in a diene synthesis. The reac-

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(11) J. L. Melles and H. J. Backer, *Rec. trav. chim.*, **72**, 491 (1953).

(12) C. F. H. Allen and J. A. van Allen, THIS JOURNAL, **72**, 5165 (1950).

(13) (a) K. Alder and G. Stein, *Ann.*, **485**, 223 (1931); (b) H. Staudinger and A. Rheiner, *Helv. Chim. Acta*, **7**, 27 (1924).

(14) The authors are indebted to Vivian Kapuscinski, James French, Robert Keen and Arthur Tomasewski for the analyses. All melting points are corrected.

(15) K. Alder, H. F. Rickert and E. Windemuth, *Ber.*, **71**, 2451 (1938).

tion mixture was purified by trituration with petroleum ether rather than by distillation. Concentration and cooling of the combined petroleum ether triturates gave a 25% yield of Δ^5-hexahydrobenzothiophene 1-dioxide as pure white needles, m.p. 92.5–94°. (Alder, Rickert and Windemuth[15] reported m.p. 94–95° and no yield.)

Octahydrobenzothiophene 1-Dioxide (III). **A. By Hydrogenation of 3a,7a-Dihydrobenzothiophene 1-Dioxide** (II).—A solution of 0.35 g. (0.0021 mole) of 3a,7a-dihydrobenzothiophene 1-dioxide (II) in 50 ml. of glacial acetic acid, plus 0.1 g. of prereduced PtO_2, was subjected to low pressure hydrogenation. The hydrogen up-take was 140 ml. (0° and 760 mm.) (100% of theory) in 22 minutes. The catalyst was filtered off and the filtrate evaporated to dryness to give a dark red oil. Purification with neutral charcoal produced a light yellow oil. Recrystallization from an ether–petroleum ether mixture gave 0.31 g. (86%) of pure white needles of octahydrobenzothiophene 1-dioxide (III), m.p. 39–40°.

Anal. Calcd. for $C_8H_{14}O_2S$: C, 55.17; H, 8.05. Found: C, 55.02; H, 8.17.

B. **By Hydrogenation of Δ^5-Hexahydrobenzothiophene 1-Dioxide** (VII).—A solution of 0.22 g. (0.00128 mole) of Δ^5-hexahydrobenzothiophene 1-dioxide (VII) in 50 ml. of glacial acetic acid, plus 0.1 g. of prereduced PtO_2, was subjected to low pressure hydrogenation. After the reaction had proceeded for one-half hour with the up-take of one equivalent of hydrogen, the catalyst was filtered off and the filtrate evaporated to dryness to give a light yellow oil. Two recrystallizations from an ether–petroleum ether mixture gave 0.20 g. (90%) of pure white needles of octahydrobenzothiophene 1-dioxide (III), m.p. 39–40°. A mixed melting point determination with a sample prepared by hydrogenation of II described above showed no depression.

C. **By Hydrogenation of Dibromotetrahydrobenzothiophene 1-Dioxide (XIXb).**—Hydrogenation of 0.0535 g. (0.00016 mole) of dibromotetrahydrobenzothiophene 1-dioxide (XIXb) in acetic acid over PtO_2 resulted in the up-take of four equivalents of hydrogen and the isolation of 0.021 g. (77%) of octahydrobenzothiophene 1-dioxide (III), m.p. 37–38°. Mixed melting point with an authentic sample of octahydrobenzothiophene 1-dioxide (III) prepared above showed no depression.

Dibromotetrahydrobenzothiophene 1-Dioxide (XIXa). A. **By Bromination of Thiophene 1-Dioxide** (I).—To the cold chloroform extracts containing 5.04 g. (0.0434 mole; assuming a 66% yield from 0.066 mole of 3-dimethylamino-2,3-dihydrothiophene 1-dioxide methiodide) of thiophene 1-dioxide (I) was added 18 g. (0.111 mole) of bromine in five portions, diluted with small amounts of chloroform, over a 48-hour period. All the previously added bromine was allowed to react before the subsequent addition was made. (The trace of trimethylamine in the reaction solution caused an immediate decoloration of the first small portion of bromine.) The chloroform solution was decanted from a small amount of insoluble oil and washed with sodium thiosulfate solution to remove the small amount of unreacted bromine. Since the chloroform solution was found to be acid at the end of the bromination reactions, the resulting light yellow chloroform layer was washed with sodium bicarbonate solution to remove any traces of hydrobromic acid. The chloroform solution was then washed twice with distilled water, dried over magnesium sulfate, filtered and evaporated to dryness under a slight vacuum, while the pot temperature was maintained below 28°, to yield 9.92 g. of light yellow oil containing a small amount of solid material.

This crude oil was taken up in chloroform, saturated with ether or petroleum ether at room temperature, and cooled. Invariably, oils were obtained, but upon standing in the icechest for a period of time, a solid formed which was mixed with considerable oil. The oily portion could be removed by rapid washing with chloroform to give the solid material as a powder or large, poorly defined crystals. It was finally possible to isolate five fractions of crystalline product, weighing 2.97 g., and having melting points ranging from 90–124°. The higher melting fractions were combined and partially purified by crystallization from chloroform–ether–petroleum ether solutions, giving a product which still had a very wide melting point range. However, rapid recrystallization from a water–ethanol mixture gave a dibromotetrahydrobenzothiophene 1-dioxide (XIXa), melting at 157–158°. Cold silver nitrate slowly gave a precipitate with XIXa, indicating an allylic bromine, and the ultraviolet absorption indicated the presence of an α,β-unsaturated sulfone. (The same product was not obtained when the crude substance was in contact with warm ethanol–water for a number of hours.)

Anal. Calcd. for $C_8H_8O_2SBr_2$: C, 29.27; H, 2.44. Found: C, 29.50; H, 2.68.

B. **From 3a,7a-Dihydrobenzothiophene 1-Dioxide** (II).—A solution of 0.10 g. (0.00060 mole) of 3a,7a-dihydrobenzothiophene 1-dioxide (II) in 5 ml. of chloroform was treated with 0.20 g. (0.00126 mole) of bromine in 2 ml. of chloroform in two equal portions. The first 0.10 g. (0.00063 mole) of bromine was absorbed almost instantaneously, while the second portion was unabsorbed after 1 hour (by comparison with a visual standard).

The reaction mixture was diluted to 100 ml. with more chloroform and washed with aqueous sodium thiosulfate solution and then with water. The chloroform layer was dried over magnesium sulfate, filtered, and evaporated to dryness at room temperature to give 0.20 g. of a honeycomb-like solid. Recrystallization from a chloroform–ether–petroleum ether mixture gave 0.19 g. (95%) of pure white needles of a dibromotetrahydrobenzothiophene 1-dioxide (XIXa), m.p. 156–158°. Mixed melting point with a sample of XIXa prepared above showed no depression.

Dibromotetrahydrobenzothiophene 1-Dioxide (XIXb). A. **By Bromination of Thiophene 1-Dioxide** (I).—The medium and high melting fractions isolated above from the bromination of thiophene 1-dioxide (I) were recrystallized several times from hot dilute alcohol to give a second isomeric dibromotetrahydrobenzothiophene 1-dioxide (XIXb), m.p. 127–128°. XIXb reacted much faster with silver nitrate than did XIXa, indicating that the two compounds were indeed isomeric and not polymorphic modifications. Ultraviolet absorption again indicated the presence of an α,β-unsaturated sulfone. It was not determined which of the three possible dibromotetrahydrobenzothiophene 1-dioxides, XIXc, XIXd or XIXe, are represented by these two isomers XIXa and XIXb.

Anal. Calcd. for $C_8H_8O_2SBr_2$: C, 29.27; H, 2.44; mol. wt., 328. Found: C, 29.26; H, 2.75; mol. wt. (cryoscopic in benzene), 316.

B. **By Isomerization of Dibromotetrahydrobenzothiophene 1-Dioxide (XIXa).**—Heating under reflux 0.33 g. (0.001 mole) of dibromotetrahydrobenzothiophene 1-dioxide (XIXa), m.p. 157–158°, in dilute alcohol for 2 hours, followed by recrystallization, produced 0.24 g. (73%) of the isomeric dibromotetrahydrobenzothiophene 1-dioxide (XIXb), m.p. 127–128°. Mixed melting point with a sample of XIXb obtained from bromination of thiophene 1-dioxide (I) showed no depression.

2,3-Dibromo-2,3-dihydrothiophene 1-Dioxide (XVIII).—Recrystallization of the lower melting fractions resulting from the bromination of thiophene 1-dioxide (I) produced 2,3-dibromo-2,3-dihydrothiophene 1-dioxide (XVIII), m.p. 98–99°. XVIII did not react with cold alcoholic silver nitrate and reacted only very slowly with the hot reagent, resembling the behavior of 3-bromo-2,3-dihydrothiophene 1-dioxide (XX).[2] In addition, the ultraviolet absorption spectra of XVIII and XX were almost identical.

Anal. Calcd. for $C_4H_4O_2SBr_2$: C, 17.39; H, 1.45; Br, 57.97; mol. wt., 276. Found: C, 17.67; H, 1.70; Br, 57.70; mol. wt. (cryoscopic in benzene), 273.

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